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(71) Applicant (for all designated States except US): STY-
ROPHEN INTERNATIONAL PTY LTD [AU/AU]; 17
Murray Road, Point Lonsdale, Victoria 3225 (AU).

(72) Inventors; and

(75) Inventors/Applicants (for US only): QUIST, Ingmar
[AU/AU]; 3/7 Westley Street, Carrum, Victoria 3197 (AU).
JOHN, Anthony, Jacob [AU/AU]; 19 President Road, St
Albans, Victoria 3021 (AU).

(74) Agent: FREEHILLS CARTER SMITH BEADLE;
Level 43, 101 Collins Street, Melbourne, Victoria 3000
(AU).

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(54) Title: POLYMERIC COMPOSITE FOAM

(57) Abstract: A polymeric composite foam is disclosed where the continuous phase is a foamed phenolic/furan polymer and the disperse phase is a foamed polystyrene polymer. The composite has a preferred density in the range 25 - 50 kg/m³ and the composites exhibit good thermal insulation and fire resistant properties. The process for preparing the composites is relatively low cost.



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POLYMERIC COMPOSITE FOAM

Technical Field

This invention relates to polymeric composite foams. The invention also relates to liquid compositions for preparing polymeric composite foams and
5 insulating panels formed from these foams.

Background to the Invention

Polymeric foams are widely used for thermal and acoustic insulation in building construction. Polymeric foams such as polystyrene foams are widely used as a core enclosed within sheets of steel to form insulation panels for cool rooms
10 and factories because of their excellent mechanical properties, high insulation value and low cost. The main negative feature of these insulation panels is their high propensity to burn and/or melt in a fire leading to the loss of structural strength. Phenolic and furan foams, on the other hand have excellent fire resistance properties, but are not able to be used as the core in steel clad panels because of
15 their poor mechanical properties. They are extremely rigid and form a friable surface when cut.

A further problem with phenolic and furan foams is achieving satisfactory adhesion to the steel sheets.

United Kingdom patent application GB 2013209A discloses a method of
20 forming panels of a polycondensable resin. The invention of this citation dissociates the expansion or foaming of the resin from its polymerisation or polycondensation. This means that expansion occurs before polymerisation or hardening of the resin. The method requires external heating as expansion is required to take place before polymerisation. The composition may include
25 polystyrene beads. However, these are used in expanded form as the polycondensation reaction takes places at approximately 60°, a temperature too low to allow the polystyrene beads to expand. To expand polystyrene beads temperatures close to the softening point or glass transition temperature of polystyrene are required. This citation has a complex heating regime to overcome
30 the problems perceived from having curing/polymerisation processes linked. It is

for this reason that the foaming and curing/polymerisation of the polycondensable phase are separated and why expanded polystyrene beads are used.

Belgium patent application BE 865001 is similar to the UK patent discussed above as the composite foam is prepared using expanded polystyrene beads. The heating in their process is limited to temperatures less than that required for deformation of the polystyrene particles.

USSR patent application SU 585189 also discloses compositions that involve the use of expanded polystyrene beads.

German patent application DE 19910257 discloses fire resistant polymer foam compositions that include 5-50 wt % of expandable graphite. The compositions are prepared by adding the liquid mixture to a mould and heating by external steam. Both examples use expanded polystyrene beads and the weight ratio of phenolic resin to polystyrene is less than 0.5.

Summary of the Invention

This invention provides in one form a polymeric composite foam comprising a continuous phase of foamed phenolic or furan (phenolic/furan) polymer and a disperse phase of foamed polystyrene polymer wherein the composite foam is prepared by catalysing a liquid foamable composition comprising 5-50% w/w of foamable polystyrene beads and 50-95% of a phenolic/furan resin wherein the said catalysed foamable composition is capable of achieving temperatures sufficient to polymerise the phenolic/furan polymer and expand the polystyrene polymer without requiring the application of external heat or energy sources.

Preferably the weight percent of polystyrene polymer in the composite foam is in the range 5-50 and more preferably 10-40.

Preferably the composite foam has a density in the range 25 – 200 kg/m³.

Preferably the composite foam has a density in the range 25 – 50 kg/m³.

Preferably the composite foam has a density in the range 50 – 200 kg/m³.

In an alternative form the invention provides a steel clad insulation panel having a core of composite foam comprising a continuous phase of phenolic/furan polymer and a disperse phase of foamed polystyrene polymer wherein the weight ratio of phenolic/furan polymer to polystyrene is at least 1.

In a further alternative form the invention provides a method of forming a mass of polymeric composite foam comprising adding a liquid foamable composition comprising 5-50% w/w of foamable polystyrene beads and 50-95% of a phenolic/furan resin and an effective amount of a catalyst to a temporary mould in the shape of the mass and removing the mould after the liquid composition commences to expand.

Detailed Description of the Invention

The resins suitable for this invention are synthetic thermosetting resins. They may be obtained, for example, by the condensation of phenol, substituted phenols or furfuryl alcohol with aldehydes such as formaldehyde, acetaldehyde and furfural. However, as appreciated by those skilled in the art, phenol may be replaced, wholly or in part, by other substances with phenol-like chemistry, such as substituted phenols, cresol or natural phenolic compounds such as lignin or tannin. Tannin, in particular is a reactive substance that can be used in significant quantities as a low cost resin extender in the present invention. Furfuryl alcohol may be replaced by other reactive compounds containing the furan molecular structure, i.e. a ring formed by four carbon and one oxygen atom. The ring can have zero, one or two double bonds, preferably two as this makes the compound more reactive and more likely to form a char when exposed to high temperature. Formaldehyde may be replaced by other aldehydes, but these are generally more expensive and less reactive, and thus not preferred. Phenol-formaldehyde resins constitute the main class of phenolic resins suitable for the present invention. They are usually prepared by the reaction of phenol with aqueous 37-50% formaldehyde at 50-100°C in the presence of a basic catalyst.

The phenolic resins that are most useful in the present invention are referred to as phenol-aldehyde resins and generally containing one phenol and one aldehyde component. Two general types of phenolic resins that are well known in the art are the novolaks and the resols.

As general rule, liquid resol resins are prepared by reacting one or more phenols with an excess of one or more aldehydes in aqueous phase and in the

presence of an alkaline catalyst. The excess of aldehyde may be small or large depending on the type of resin required.

Novolaks are usually prepared by reacting excess amounts of phenol with formaldehyde. The novolak resin molecule is built up from
5 dihydroxyphenylmethane which upon further addition of formaldehyde and immediate condensation of alcohol groups thus formed with another phenol molecule gives linear compounds having the general formula $H[C_6H_3(OH).CH_2]_n$ $C_6H_4.OH$ as well as branched polymers in which some of the benzene rings have three methylene bridge attachments under acidic conditions. Novolaks can also be
10 made under alkaline conditions and both types of novolaks can be incorporated into a resol, made separately or in-situ for the purpose of producing phenolic foams.

The term phenol can include not only phenol itself (including pure and technical grade phenol) but also other phenol compounds such as resorcinol, cresol, xlenol, chlorophenol, bisphenol-A, .alpha.-naphtol, β -naphtol and the like, and
15 admixtures thereof.

Furan resins are defined for the purpose of this application as liquid resins that contain at least 10% w/w of compounds whose molecular structure incorporates the furan ring, with zero, one or two double bonds; and which can be cured by heat or the addition of an acid catalyst, to form a thermoset solid

20 The furan resin preferably contains some furfuryl alcohol, or reaction products of furfuryl alcohol, e.g. those described in US Patent 5,545,825.

Aldehydes to be used for reaction with the above-mentioned phenols or furfuryl alcohol usually contain about 1 to 8 carbon atoms and preferably about 1 to 3 carbon atoms. Specific examples of aldehydes include formaldehyde,
25 acetaldehyde, propionic aldehyde, furfural, benzaldehyde and the like, and admixtures thereof. In the context of the present invention, the use of formaldehyde is preferred. The most common commercially available forms of formaldehyde include formalin which is usually a 30-52% by weight aqueous solution of formaldehyde in water; paraformaldehyde, which is a solid linear polymer of
30 formaldehyde; and trioxane, which is a solid cyclic tripolymer of formaldehyde.

The above and other sources of formaldehyde for reaction with phenol or furfuryl alcohol are intended to be embraced herein when the term formaldehyde is used.

Surfactants may be used and are selected from any suitable stabilising agent useful in stabilising liquid phenol-aldehyde resin foams. The surfactant can be
5 anionic, cationic, non-ionic or amphoteric. The major restriction is that it must not interfere with the foaming process. A large number of suitable surfactants are known and are disclosed in numerous publications. Commonly used surfactants include silicon surfactants such as siloxane-oxyalkylene co-polymers and organic
10 surfactants such as polyethers and polyalcohols, including their condensation products and alkylene oxides such as ethylene oxides and propylene oxides, with alkyl phenols, fatty acids, alkylsilanes and silicones. Specific examples include polyoxyethylene octadecylphenol, polyoxyethylene decylphenol sulphate, polyoxyethylene dodecyl phenol, polyoxyethylene octyl phenol, polyoxyethylene linoleic acid ester, polyoxyethylene stearic acid ester, polyoxyethylene sorbitan
15 monolaurate, polyoxyethylene sorbitan tristearate.

The amount of surfactant used is usually not critical as small amounts, 1% or less by weight of resin, often result in a substantial reduction in the surface tension of the resin.

Typical blowing agents which may be employed in preparing the phenolic or
20 furan foam component of the present invention include physical and chemical blowing agents as well as mechanical blowing techniques. In a preferred embodiment the blowing agent is provided by the water in the resin, which is either present in the resin as prepared or generated in the curing process. While it is preferred, it is not essential that the phenolic resin or furan resin is foamable.
25 However, for cost reasons and thermal properties, it is preferred that the phenolic resin or furan resin is foamable.

Typical acid catalysts include phosphoric acid, alkane sulphonic acids such as methane sulphonic acid, hydrochloric acid and sulphuric acid, or blends thereof. Suitable acids are those used in the art for curing phenolic resins. They are usually
30 characterised as strong acids. The catalysts may also be selected from aromatic sulphonic acids such as phenol sulphonic acid, benzene sulphonic acid, toluene

sulphonic acid and xylene sulphonic acid. Lewis acids such as aluminium chloride may also be used.

In most instances, the acid catalyst is added in amounts sufficient to reduce the initial pH of the liquid resin mixture below 4, preferably between 1.5 and 3.0.

- 5 Also, the amount of catalyst needed can be determined by evaluating the desired cream times and firm times of the reaction mixture. Generally speaking, however, the concentration of catalyst contained in the foaming reaction mixture will vary between 5 and 20 w/w % of phenolic/furan resin. The catalyst converts the resin to polymer.

- 10 The liquid resin composition must have a suitable reactivity, meaning it must generate enough heat in an exothermic chemical reaction to cause the expandable polystyrene beads to expand. This expansion process will normally not occur unless the temperature of the resin reaches a temperature of at least 80°C, preferably at least 90°C, most preferably at least 100°C.

- 15 By reaching a particular temperature after catalysis it is meant that when 1000g of foamable resin is placed in a 10 litre cylindrical container of diameter 200mm that temperature is reached after catalysis. This feature of the present invention provides the advantage that panels may be prepared with relatively simple and inexpensive equipment. External heat sources such as steam or microwaves are
20 generally not necessary. However, such external heat sources may be used to prepare the compositions of the present invention.

- Additives that increase the heat generated by the catalysed resin can beneficially be added, for example furfuryl alcohol or peroxides, preferably hydrogen peroxide on account of its high reactivity and low cost. It will be
25 appreciated that the use of such additives is to be taken into account as to whether a resin is suitable in terms of meeting the exotherm test.

- Other additives may be included, such as those described in prior art foams, to improve any particular physical property or to reduce costs. For example, fire retardants containing eg. chlorine, bromine, boron, phosphorous or ammonia
30 especially ammonium phosphate may be added to improve fire resistance. Expandable graphite can also be usefully employed, for example as described in DE

19910257A1. The graphite expands when exposed to high temperatures as encountered in a fire. The same patent application also describes the use of intumescent additives, e.g. a mixture of melamine, a PVA co-polymer, pentaerythritol and ammonium phosphate. These and other additives with similar
5 effect may be incorporated in the compositions of the present invention. Low cost fillers such as perlite, fly ash, and vermiculite may be added to reduce cost. Such fillers may also be beneficial in that they can act as nucleating agents, reducing the average cell size of the resin foam component. Urea, melamine and other nitrogen containing compounds capable of reacting, like phenol and furfuryl alcohol, with
10 aldehydes in a two-stage reaction known in the art as addition followed by condensation, can also be used on their own or as reaction products with aldehydes, preferably formaldehyde, to replace some of the phenolic or furan resins. Neutralising agents may be added to the foamable mixture, such as slow dissolving salts like anhydrous borax. The methods described in US Patent 4,122,045 are
15 hereby incorporated into this specification.

The polystyrene polymer suitable for the present invention includes styrene polymers that are commonly used for preparing polystyrene beads that are to be blown to form polystyrene foam beads. As well as using styrene as the sole monomer other addition polymerisable monomers may be used and such
20 copolymers are embraced by the term polystyrene in this specification. Styrene is always present as the major component of the polystyrene polymer. Furthermore, the polystyrene polymers may be modified by the addition of fire retardants. Preferred polystyrene beads contain flame retardants such as beads supplied by Huntsman under the trade name Spacel 4940 and Spacel 7740.

25 The present invention involves the use of unexpanded polystyrene beads. This enables relatively high levels of polystyrene to be incorporated into the final foam composite as the rheology and flow properties of the liquid compositions is much more manageable. If expanded polystyrene beads were used only relatively low levels of polystyrene could be incorporated into the composite foam when a
30 pourable mixture is used.

The preferred polystyrene blowing agent and technique comprise the employment of liquid physical blowing agents, the agents which are volatile liquids which produce a blowing gas through vaporisation of the blowing agent or through decomposition of the blowing agent during the exotherm.

- 5 Numerous blowing agents suitable for use in the context of the present invention are well known in the prior art. Ideally, the blowing agent should be a liquid having an atmospheric pressure boiling point between -50° and 100° C. and more preferably between 0° and 50° C.

10 Examples of volatile blowing agents include organic compounds such as hydrocarbons, halogenated hydrocarbons, alcohols, ketones and ethers. Specific examples of hydrocarbon blowing agents include propane, pentane, isopentane and hexane. Pentane is the preferred blowing agent.

The blowing agents are employed in an amount sufficient to give the resulting polystyrene foam the desired density. In the case of the present invention
15 it has been found particularly useful to employ expandable polystyrene beads that expand to a density of about $13\text{--}20\text{ kg/m}^3$ when conventionally blown with steam in a single pass process. In this specification and in accordance with industry practice, this density refers to the density of packed expanded beads of polystyrene. To allow for packing volume, the actual density of these expanded beads is
20 approximately 50% greater, that is approximately $20\text{--}30\text{ kg/m}^3$. In the present invention the density of the phenolic foam phase is preferably at least twice that of the polystyrene foam and in expressing this ratio we refer to the actual densities of the two phases. Lower density phenolic foams offer the advantage of lower cost but poorer mechanical properties. For general purpose insulation panels, foam in
25 the density range $25\text{--}50\text{ kg/m}^3$ normally provides adequate strength, but even lower densities may be useful. For applications requiring maximum fire resistance and/or structural strength, higher density may be preferred, for example, $50\text{--}200\text{ kg/m}^3$, or higher.

The relative weight proportions of the polystyrene polymer phase and
30 phenolic/furan polymer phase are important to the present invention. In this specification the relative proportions are calculated by reference to the composition

of the liquid foamable composition. In making these calculations the phenolic/furan phase includes all additives such as catalysts, fillers, water, surfactants and fire retardants and only excludes the polystyrene beads. It will be appreciated that the actual relative weight proportions of the polystyrene polymer phase and phenolic/furan polymer phase in the composite foam may vary slightly from the relative weight proportions calculated as above. These differences may be accounted for by the loss of volatile components. However, the above method is used for convenience.

A feature of the present invention that sets it apart from other rigid foams such as phenolic, polyurethane and expanded polystyrene (EPS) is the ability of the pre-rise foam mixture to retain a "memory" of its shape, to produce a final, fully expanded article with approximately the same shape as the pre-rise foamable mixture. "The same shape" means the ratio of length : width : height is about the same for the final, expanded foam as for the pre-rise mixture. A highly beneficial feature of this "memory" of pre-rise shape is the fact that the foam can be produced with extremely simple and thus low cost equipment. For example, a cardboard box, as used for packaging, can be used as a temporary mould to produce commercial size blocks. In such case, the four vertical corners of the box should be slit, allowing all vertical sides to be folded out to become horizontal, resting on the floor. The four sides of the box should be held in a vertical position (i.e. forming a box) only long enough to allow the foamable mixture to be poured into the box, and the rise or expansion to commence.

Following the commencement of the rise, the four vertical sides of the box can be folded out to become horizontal, allowing the foam to expand in all three dimensions, while maintaining approximately the initial shape, i.e. the ratio of length : width : height. The use of this dismantable or collapsible box or mould is an example of the use of a temporary mould. Further examples of temporary moulds are trays formed by frangible or meltable walls. After the foamable composition has begun to exotherm, a temperature or pressure is reached where the wall melts, weakens or ruptures such that the expanding foamable composition is no longer confined by the walls of the temporary mould. When the expanding

foamable composition is no longer confined by the walls, the walls are regarded as being removed. Removal of the walls may be achieved by melting or breaking as well as by physical intervention by an operator. The walls of the dismantable or collapsible box may alternatively be held in the shape that defines the mould by
5 meltable retaining means. When the foamable composition exotherms and expands it reaches a predetermined temperature that causes the retaining means to break and the walls of the mould to fall outwards, allowing the expanding mass to be not confined. A temporary mould, i.e. a device that spatially confines the catalysed liquid foamable composition only until the expansion commences, can also
10 beneficially be used in continuous lines, for example, in the production of continuous blocks. In this case, the temporary mould can be created, for example, by mechanically folding paper feeding off a roll, into a trough-like shape that confines a suitable amount of the catalysed liquid composition only long enough for the expansion to commence.

15 In a variation of the above process, the temporary mould containing the catalysed liquid foamable composition may be placed in a second or outer mould. This outer mould may be open on one face or totally enclosed. We have found that by using a temporary mould within an outer mould that the final faces of the composite foam are more uniform and reproducible and thus require less trimming.

20 Remarkably, using this simple method, allowing the bulk of the expansion of the foam to take place without any spatial constraints, blocks of commercially useful size can be produced i.e. in excess of 1m^3 . This is in contrast to other plastic block foams, which require spatial confinement in at least two dimensions (phenolic and polyurethane foams) and often three dimensions (expanded polystyrene foam
25 EPS). In the case of EPS, there is additionally a requirement for an external supply of pressurised steam, adding to the complexity and cost of the production equipment.

While the simple method described above can be used to produce blocks of foam of the invention, the foam can also be produced in a confined space, provided
30 the mould is strong enough to withstand the pressure exerted by the expanding foam. The foam of the invention can also be produced on continuous lines. One of

the significant advantages of the present invention is that external heat or energy sources are not necessary. It is surprising that composite foams can be prepared where the exothermic heat of reaction from the polymerisation of one polymeric phase can be used to foam not only this phase but the other polymer phase. This is
 5 contrary to the prior teaching discussed earlier where the separation of these roles is considered essential. The prior art generally uses expanded polystyrene beads and relies on external heat being applied. The invention will be further described by reference to preferred embodiments in the following examples.

Example 1

10 A foamable mixture was prepared using the following formulation where perlite was included as a nucleating agent to assist in the foaming of the phenolic resin.:

	Phenolic resin, grade IL1737 ex Huntsman	1000g
	Polystyrene beads, grade Spacel 4940 ex Huntsman	200g
15	Furfuryl Alcohol	100g
	Teric C12 (surfactant) ex Huntsman	40g
	Perlite	10g
	75% phenol sulphonic acid, }	140g
	} Premix	
20	85% phosphoric acid	60g

In a 10 litre bucket, all above components except the acid blend were mixed together and warmed to 30°C. The acid catalyst blend was added, and the whole mixture stirred vigorously for 30 seconds. In less than 1 minute, the liquid mixture started to expand rapidly and the temperature of the mixture reached 100°C. In a
 25 short period of time, a plastic body of foam was created, with an approximate volume of 9 litres. On the same day a sample was cut from the foam, weighed and measured and found to have a density of 151kg/m³. Expanded polystyrene beads were clearly visible on all cut surfaces, having a diameter mostly in the range 1 to 2mm. The estimated average size was 1.5mm, corresponding to a volume of
 30 1.8mm³. As the average volume of the unexpanded polystyrene beads was only about 0.05mm³, the average expansion was 36 times the original volume. Thus, as

the specific density of the unexpanded polystyrene beads was 1000kg/m^3 , the average specific density of the expanded beads was calculated to be 28kg/m^3 . As the weight percentage of polystyrene in the mixture was $200\text{g}:1550\text{g} = 13\%$, it follows that the weight component of polystyrene would be 13% of $151\text{kg/m}^3 =$
 5 20kg. The weight percent of the phenolic/furan polymer phase was calculated to be 87%. As the average specific density of the expanded polystyrene beads was previously calculated to be 28kg/m^3 , the weight 20kg per m^3 would represent a volume of $20:28\text{m}^3 = 0.71\text{m}^3$ ie. a volume fraction of 71%.

The cut foam surface was not friable like prior art phenolic foams, yet the
 10 foam would not melt and burn like polystyrene foam when subjected to a flame.

Example 2

This example illustrates the effect of higher polystyrene content

A foamable mixture was prepared using the following formulation:

	Phenolic resin, grade IL - 1737 ex Huntsman	1000g
15	Polystyrene beads, grade Spacel 4940 ex Huntsman	400g
	Furfuryl Alcohol	100g
	Teric C12 (surfactant) ex Huntsman	40g
	Perlite	10g
20	75% phenolsulphonic acid	140g
	} Premix	
		85% phosphoric acid
		60g

In a 10 litre bucket, all above components except the acid blend were mixed together and warmed to 30°C . The acid catalyst blend was added, and the whole mixture stirred vigorously for 30 seconds. In less than 1 minute, the liquid mixture
 25 started to expand rapidly and the temperature of the mixture reached 100°C . In a short period of time, a plastic body of foam was created, with an approximate volume of 14 litres. A sample was cut from the foam on the same day, weighed and measured and found to have a density of 98kg/m^3 . A multitude of expanded polystyrene beads were clearly visible on all cut surfaces, having a diameter mostly
 30 in the range 1 to 2mm, with an estimated average of 1.5mm.

The weight percentage of polystyrene in the mixture was calculated to be

23%, and the volume percentage to be 81%. The weight percent of phenolic/furan polymer was calculated to be 77%.

The cut foam surface was not friable like prior art phenolic foams, yet the foam would not melt and burn like polystyrene foam when subjected to a flame.

5 Example 3

This example shows the effect of a higher level of furfuryl alcohol, resulting in more expansion and thus a lower density of foam. This example also illustrates the use of a furan resin.

Phenolic resin, grade 1L – 1737 ex Huntsman	1000g
Polystyrene beads, grade Spacel 4940 ex Huntsman	400g
Furfuryl Alcohol	150g
Teric C12 (surfactant) ex Huntsman	40g
Perlite	10g
75% phenol sulphonic acid	140g
} Premix	
85% phosphoric Acid	60g

10 In a 10 litre bucket, the resin, polystyrene beads, furfuryl alcohol, Teric C12 and Perlite were mixed, and the mix warmed to 30°C. The acid catalyst blend was then added, and the whole mixture stirred vigorously for 30 seconds. In less than 1 minute, the liquid mixture started to expand rapidly and the temperature of the mixture increased to 103°C. In a short period of time a plastic body of foam was created with an approximate volume of 20 litres.

15 A sample was cut from the foam on the same day, weighed and measured and found to have a density of 74kg/m³. Four weeks later the sample was weighed again, showing a weight loss of 10% corresponding to a mature density of 67 kg/m³. It is likely that the weight loss was made up mostly of excess moisture and possibly the pentane blowing agent in the polystyrene beads. Expanded polystyrene
20 beads were clearly visible on all cut surfaces, having a diameter mostly in the range 1.0 to 2.5 mm with an estimated average size of 1.5 mm, corresponding to a volume of 1.8 mm³. As the average volume of the unexpanded polystyrene beads was only about 0.05 mm³, the average expansion was 36 times the original volume. Thus, as

the specific density of the unexpanded polystyrene beads was 1000 kg/m^3 , the average specific density of the expanded beads was calculated to be 28 kg/m^3 . As the weight percentage of polystyrene in the mixture was $400\text{g} : 1800\text{g} = 22\%$, it follows that the weight component of polystyrene would be 22% of 74kg/m^3 . As
 5 the specific density of the expanded polystyrene beads was previously calculated to be 28kg/m^3 , the weight 16kg should represent a volume of $\frac{16}{28} = 0.57\text{m}^3$, ie. volume fraction of 57%.

Thus, expressed in terms of both weight and volume ratios, the composite foam could be described as comprising a polystyrene foam phase representing 22%
 10 by weight but 57% by volume, and a phenolic/furan foam phase representing 78% by weight but only 43% by volume. The phenolic/furan foam component was calculated to have a specific density of $\frac{0.78 \times 74}{0.43} \text{ kg/m}^3 = 134\text{kg/m}^3$ (before loss of volatiles on aging). Thus, in this case, the density of the phenolic/furan foam component was found to be $\frac{134}{28} = 4.8$ times higher than the polystyrene foam
 15 density.

The cut foam surface was not friable like prior art phenolic foams, yet the foam would not melt and burn like polystyrene foam when subjected to a flame. This is surprising considering that about three quarters of the volume of the composite foam was made up of polystyrene foam, which on its own immediately
 20 melts and then burns, when subjected to a flame.

Example 4

This example shows that it is possible to foam a phenolic resin without the presence of a surfactant.

Phenolic resin Cascophen PA 2027 ex Borden	1000g
Spacel 4940 ex Huntsman	600g
75% phenolsulphonic acid	80g
} Premix	
85% phosphoric acid	60g

In a 10 litre bucket, the resin and polystyrene beads were mixed and warmed

to 30°C. The acid catalyst blend was added, and the whole mixture stirred vigorously for 30 seconds. In less than 1 minute, the liquid mixture started to expand rapidly, and the temperature of the mixture increased to 102°C. In a short period of time, a plastic body of foam was created with an approximate volume of 22 litres. A sample was cut from the foam, weighed and measured and found to have a density of 61kg/m³. Four weeks later the sample was weighed again, showing a weight loss of 10% corresponding to a mature density of 55kg/m³. It is likely that the weight loss was made up mostly of excess moisture and possibly the pentane blowing agent in the polystyrene beads.

Expanded polystyrene beads were clearly visible on all cut surfaces, having a diameter mostly in the range 1.0 to 2.5 mm. The estimated average size was 1.5mm, corresponding to a volume of 1.8mm³. As the average volume of the unexpanded polystyrene beads was only about 0.05mm³, the average expansion was 36 times the original volume. Thus, as the specific density of the unexpanded polystyrene beads was 1000kg/m³, the specific density of the expanded beads was calculated to be 28kg/m³. As the weight percentage of polystyrene in the mixture was 600g : 1740g = 34%, it follows that the weight component of polystyrene would be 34% of 61kg/m³ = 21kg/m³. As the specific density of the expanded polystyrene beads was previously calculated to be 28kg/m³, the weight 21kg should represent a volume of $\frac{21}{28} = 0.75\text{m}^3$, ie. a volume fraction of 75%.

Thus, expressed in terms of both weight and volume ratios, the composite foam could be described as comprising a polystyrene foam phase representing 34% by weight but 75% by volume, and a phenolic foam phase representing 66% by weight but only 25% by volume. The phenolic foam component was calculated to have a specific density of $\frac{0.66 \times 61}{0.25} \text{kg/m}^3 = 161\text{kg/m}^3$ (before loss of volatiles on aging). Thus, in this case, the density of the phenolic foam component was found to be $\frac{161}{28} = 5.8$ times higher than the polystyrene foam density.

The cut foam surface was not friable like prior art phenolic foams, yet the foam would not melt and burn like polystyrene foam when subjected to a flame.

This is surprising considering that three quarters of the volume of the composite foam was made up of polystyrene foam, which on its own, immediately melts and then burns when subjected to a flame.

Example 5

- 5 This example shows that the process of the present invention can be used to produce composite foam of very low density, i.e. less than 30 kg/m³.

Phenolic resin, grade IL1737 ex Huntsman	3,000g
Furan Resin, grade NBB101 ex Foseco	1,200g
Polystyrene beads, grade Spacel 7740 ex Huntsman	3,900g
10 Ammonium Phosphate	600g
50% sulphuric acid,	270g
} Premix	
81% phosphoric acid	270g
50% hydrogen peroxide	60g

- 15 In a 25 litre bucket, lined with a plastic bag, the phenolic resin, furan resin and polystyrene beads were mixed together and warmed to 31°C. The acid catalyst pre-mix was added, and the whole mixture stirred vigorously for 45 seconds. The plastic bag containing the mixture was then pulled out of the bucket, to allow the foam expansion to take place without major constraint. The expansion was
- 20 essentially completed in less than five minutes. After 2 hours a samples was cut and found to have density of 25kg/m³. Remarkably, even at this low density the cut foam surface was not friable like prior art phenolic foams, yet the foam would not melt and burn like polystyrene foam when subjected to a flame. This example incorporates a commercially available furan resin, a fire retardant and a peroxide,
- 25 the latter being an example of additives that increase the exothermic heat generated by the process of the invention.

Example 6

This example illustrates the ability of foam of the invention to have a "memory" of its pre-rise shape.

	Phenolic resin, grade IL1737 ex Huntsman	30,000g
	Furan resin, grade NBB101 ex Foseco	6,000g
	Polystyrene beads, grade Spacel 4940 ex Huntsman	15,000g
	Ammonium phosphate	2,700g
5	50% sulphuric acid,	2,700g
	} Premix	
	81% phosphoric acid	2,700g

Into a 100 litre drum the phenolic resin, furan resin, ammonium phosphate and polystyrene beads were added, mixed and warmed to 27°C. The acid catalyst

10 premix was added, and the whole mixture stirred vigorously for 40 seconds, then poured into a cardboard box of size 600 x 600 x 300mm (length x width x height). The box was lined with a plastic sheet, and all four vertical corners were slit, allowing the sides to be folded out to a horizontal position, i.e. resting on the floor. The four sides of the box were held in a vertical position (to form a box) until the

15 rise commenced, which occurred in less than one minute. The sides of the box were then left unsupported, and were quickly pushed out to a horizontal position by the expanding foam. Remarkably, the unsupported foam kept expanding in all directions, approximately maintaining its pre-rise shape, ending up in a fully expanded block of size 1.2 x 1.2 x 0.6m, having almost vertical sides. A sample of

20 the foam was cut and found to have a density of 42kg/m³.

Since modifications within the spirit and scope of the invention may be readily effected by persons skilled in the art, it is to be understood that the invention is not limited to the particular embodiment described, by way of example, hereinabove.

CLAIMS

1. A polymeric composite foam comprising a continuous phase of a phenolic or furan polymer and a disperse phase of foamed polystyrene polymer wherein the
5 composite foam is prepared by catalysing a liquid foamable composition comprising 5-50% w/w of foamable polystyrene beads and 50-95% of a phenolic/furan resin wherein the said catalysed foamable composition is capable of achieving temperatures sufficient to polymerise the phenolic/furan polymer and expand the polystyrene polymer without requiring the application of external heat
10 or energy sources.
2. A polymeric composite foam as defined in claim 1 wherein the weight percent of polystyrene polymer in the composite foam is in the range 5-50.
3. A polymeric composite foam as defined in claim 2 wherein the weight percent of the polystyrene polymer in the composite foam is 10-40.
- 15 4. A polymeric composite foam as defined in any one of claims 1 to 3 wherein the composite foam has a density in the range 25 – 200 kg/m³.
5. A polymeric composite foam as defined in claim 4 wherein the composite foam has a density in the range 25 – 50 kg/m³.
6. A polymeric composite foam as defined in claim 4 wherein the composite
20 foam has a density in the range 50 – 200 kg/m³.
7. A polymeric composite foam as defined in any one of claims 1 to 6 wherein the phenolic/furan polymer in the continuous phase is foamed .
8. A steel clad insulation panel having a core of a polymeric composite foam comprising a continuous phase of a phenolic/furan polymer and a disperse phase of
25 foamed polystyrene polymer wherein the weight ratio of phenolic/furan polymer to polystyrene is at least 1.
9. A steel clad insulation panel as defined in claim 8 wherein the phenolic/furan polymer is foamed.
10. A method of forming a mass of polymeric composite foam comprising
30 adding a liquid foamable composition comprising 5-50% w/w of foamable polystyrene beads and 50-95% of a phenolic/furan resin and an effective amount of

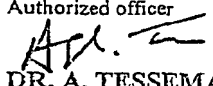
a catalyst to a temporary mould in the shape of the mass and removing the temporary mould after the liquid composition commences to expand.

11. A method as defined in claim 10 wherein the temporary mould is placed on an outer mould, which outer mould defines the shape of the composite foam after expansion.
12. A method as defined in claims 10 or 11 wherein the phenolic/furan resin is foamed.
13. A polymeric composite foam as defined in any one of claims 1 to 7 wherein the catalysed foamable composition reaches at least 80°C.
- 10 14. A polymeric composite foam as defined in claim 13 wherein the catalysed foamable composition reaches at least 90°C.
15. A polymeric composite foam as defined in claim 14 wherein the catalysed foamable composition reaches at least 100°C.
16. A polymeric composite foam as defined in any one of claims 1 to 7 and 13
- 15 to 15 comprising an additive selected from the group consisting of fire retardants, expandable graphite, intumescent agents and fillers.
17. A polymeric composite foam as defined in claim 16 wherein the fire retardant releases ammonia gas when exposed to fire.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU02/00152

A. CLASSIFICATION OF SUBJECT MATTER																						
Int. Cl. ⁷ : C08J 9/35, 9/228; C08L 61/06, 61/00, 25/06, 25/08; C08J 9/00; B29C 44/44; E04C 2/292; E04B 1/62																						
According to International Patent Classification (IPC) or to both national classification and IPC																						
B. FIELDS SEARCHED																						
Minimum documentation searched (classification system followed by classification symbols) C08J 9/35, 9/228, 9/00; C08L 61/06, 61/00, 25/06, 25/08; B29C 44/44; E04C 2/292; E04B 1/62																						
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																						
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DERWENT: WPAT JAPIO																						
C. DOCUMENTS CONSIDERED TO BE RELEVANT																						
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																				
X	US 4596682 A (MOSIER) 24 June 1986 col. 4, lines 7-28; col. 5, lines 23-33; claims	1-17																				
X	US 4714715 A (MOSIER) 22 December 1987 col. 3, line 15 - col. 4, line 63; col. 5, lines 1-3; claims 8-14	1-17																				
X	DE 19910257 A (SCHWENK DAEMMTECHNIK GMBH & CO KG) 21 September 2000 whole document	1-17																				
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex																						
* Special categories of cited documents: <table border="0"> <tr> <td>"A"</td> <td>document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T"</td> <td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E"</td> <td>earlier application or patent but published on or after the international filing date</td> <td>"X"</td> <td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L"</td> <td>document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y"</td> <td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O"</td> <td>document referring to an oral disclosure, use, exhibition or other means</td> <td>"&"</td> <td>document member of the same patent family</td> </tr> <tr> <td>"P"</td> <td>document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family	"P"	document published prior to the international filing date but later than the priority date claimed		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention																			
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																			
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																			
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"P"	document published prior to the international filing date but later than the priority date claimed																					
Date of the actual completion of the international search 20 March 2002		Date of mailing of the international search report 27 MAR 2002																				
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929		Authorized officer  DR. A. TESSEMA Telephone No : (02) 6283 2271																				

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU02/00152

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2013209 A (STRATIFORME) 8 August 1979 page 2, col. 1, line50 - col. 2, line 130; claim4	1-17
X	SU 1688577 A (PREFABRICATED BUILDINGS RES DES INST) 20 April 1996 abstract	1-7, 10-17
X	US 4992254 A (KONG) 12 February 1991 col. 3, lines 40-59; col. 4, lines 26-48; claims	1-7, 10-17
X	SU 745539 A (BASHKIR PETROL IND) 7 July 1980 abstract	1-7, 13-17
X	SU 585189 A (AS USSR GEOLOGY ORE) 27 December 1977 abstract	1-7
X	SU 453066 A (MAIN PIPELINES CONS) 15 July 1983 abstract	1-3
X	Derwent Abstract Accession Number 97-353125, Class A88, and FI 9505534 A (NESTE OY) 17 May 1995 abstract	1, 2
Y	US 4837999 A (STAYNER) 13 June 1989 col. 3, lines 15-18; col. 3, line 63 - col. 4, line 3; claims 1, 3, 6	8, 9
Y	US 5433050 A (WILSON et al.) 18 July 1995 claims	8, 9
X	Derwent Abstract Accession Number 87-318667, Class Q43, and JP 62-227934 A (MOGE) 6 October 1987 abstract	1-3
A	US 3862912 A (BERNDT et al.) 28 January 1975 whole document	1-17

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU02/00152

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
US	4596682	US	4714715	EP	237596
DE	19910257	NONE			
GB	2013209	BE	872866	CA	1128268
		DE	2856717	ES	476426
		FR	2413198	IT	1102450
		LU	80679	JP	54160484
US	4992254	US	5047225	US	5232772
US	4837999	NONE			
US	5433050	NONE			
US	3862912	BE	816764	CA	1027300
		GB	1442922	NL	7408796
		SE	7408106	FR	2235156
				NO	742078
END OF ANNEX					